(19) Europäisch s Patentamt
European Patent Office
Office eur péen des br vets

(11) Publication number: **0 131 394**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 84303999.1

(22) Date of filing: 13.06.84

(51) Int. Cl.⁴: C 11 D 1/22

(30) Priority: 07.07.83 US 512100

(43) Date of publication of application:
16.01.85 Bulletin 85/3

(84) Designated Contracting States:
AT DE FR GB IT

(71) Applicant: The Clorox Company
1221 Broadway
Oakland California 94612(US)

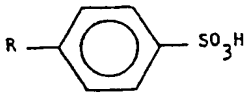
(72) Inventor: Clement, Kin-Man Choy
1929 Coventry Court
Walnut Creek California 94595(US)

(74) Representative: Goldin, Douglas Michael et al,
J.A. KEMP & CO. 14, South Square Gray's Inn
London WC1R 5EU(GB)

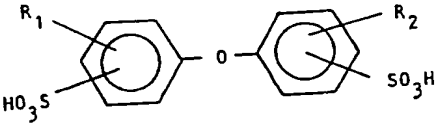
(54) Hard surface acid cleaner..

(57) Hard surface acid cleaners providing fast acting and effective cleaning results across a wide variety of problematic cleaning areas, comprise alkyl aryl sulfonic acids and at least 50.0% by weight of water.

Suitable alkyl aryl sulfonic acids are alkyl benzene sulfonic acids of the general structure



wherein R is alkyl averaging 5 to 20 carbon atoms in length and



wherein R_1 and R_2 are H or alkyl averaging 5 to 20 carbon atoms; and when R_1 is alkyl, R_2 is H.

Additionally, solvents, antimicrobial compounds, defoamers, thickeners and other cleaning adjuvants may be added to these hard surface acid cleaners.

EP 0 131 394 A2

HARD SURFACE ACID CLEANER

There are many examples of hard surface cleaners in the art, containing some sort of anionic surfactant, solvent, perhaps a dye and a fragrance to impart a pleasing color and odor, and mostly water. Most of these prior art cleaners suffer from one or more disadvantages. For example, some cleaners are effective only on hard water stains. An example of this class of cleaner is a highly acidic toilet bowl cleaner containing hydrochloric acid. Hard water stains are mineral stains caused by the deposition of calcium or magnesium salts present in hard water. Certain other cleaners may be effective only against soap scum stains, caused when a fatty acid soap, such as a sodium lauryl fatty acid soap precipitates in hard water containing alkaline earth metal salts, such as calcium, magnesium, or barium, causing the familiar soap scum stain. Still other cleaners may be effective only on greasy/oily stains. Generally speaking, these are cleaners which have either at least some water miscible solvent, and/or some higher amount of nonionic and/or anionic surfactants.

None of the prior art cleaners have addressed all three of these problematic areas together. As mentioned, a particular cleaner may be effective against a particular stain or cleaning problem, but not against the others. Thus, ineffective cleaning results may occur against certain stains using some of these cleaners, requiring purchase of other cleaners which will effectively remove the target stain. This will result in added expense as a particular cleaner must be purchased for a particular stain.

Furthermore, many of the prior art cleaners are very slow-acting. That is, after being applied to a target stain for long periods of time, they may show some cleaning effect, but this slow action is considered a great disadvantage and inconvenience.

Thus, heretofore no single cleaner has been formulated which will satisfactorily clean all three types of stains. There is also a need for an effective all purpose hard surface cleaner which is faster than the prior art cleaners. There is thus a long felt need for a multipurpose household cleaner capable of quickly and effectively cleaning all three types of stain.

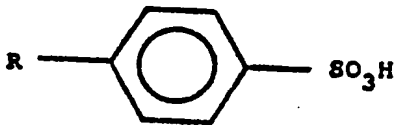
Linear alkyl benzene sulfonic acid has been well known in the detergent and cleaner field as a storage compound which, upon neutralization with generally, an alkali metal salt, is available for use as an anionic surfactant. This was recognized in Kappler, et al, U.S. 3,969,282 which utilized alkyl benzene sulfonic acid in combination with a nonionic surfactant as a storage compound to be neutralized with alkali metal salts prior to using them to launder fabrics. Further, Reid, U.S. 3,463,736 showed that linear alkyl benzene sulfonic acids could be neutralized with triethanolamine to act as a cleaner. However, it was not realized in the art that linear alkyl benzene sulfonic acids can be utilized as hard surface cleaners themselves.

This inventi n relates to an improved, hard surface acid cleaner preferably having a pH of no more than approximately 6.5 comprising:

(a) alkyl aryl sulfonic acid; and

(b) at least 50.0% by weight water.

The preferred alkyl aryl sulfonic acid is a linear alkyl benzene sulfonic acid surfactant of the general structure

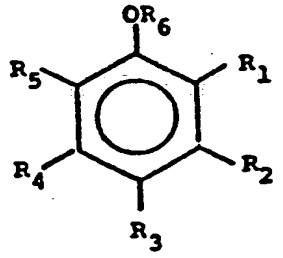


wherein R is an alkyl averaging 5 to 20 carbons.

In a further embodiment, this hard surface acid cleaner further comprises (c) a solvent selected from straight chain alkanols averaging 1 to 10 carbons, alicyclic alkanols averaging 5 to 10 carbons, dialkyl ethers averaging 2 to 8 carbons, and glycol ethers averaging 3 to 20 carbons, and mixtures thereof.

In yet another embodiment, the hard surface acid cleaner further comprises (d) an antimicrobial compound selected from:

(i) a substituted phenol of the general structure:



wherein R_1, R_2, R_3, R_4, and R_5 can separately be a phenyl group, Cl or H, and R_6 can be H or Na;

(ii) a quaternary ammonium compound; and

(iii) mixtures thereof.

In yet another embodiment, the hard surface cleaner further comprises (e) a thickener selected from gums, polysaccharides and resins.

In still another embodiment, the hard surface acid cleaner further comprises (f) a defoamer selected from the dialkyl polysiloxane polymers.

The hard surface acid cleaner of this invention can also include at least one other cleaning adjuvant selected from dyes, pigments, fragrances, and builders.

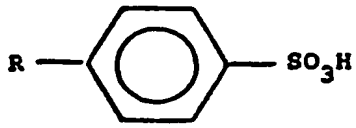
Surprisingly, the hard surface acid cleaner of this invention has proven to be both effective and fast-acting against all three major problem stains, namely, (1) soap scums; (2) hard water stains; and (3) greasy oily stains.

The present inventi n is a hard surface acid cleaner which has surprisingly effective and fast cleaning results on all three problem areas: (1) soap scums; (2) hard water stains; and (3) greasy/oily stains. The surprising revelation was that alkyl aryl sulfonic acid compounds, most specifically, linear alkyl benzene sulfonic acids, ("HLAS") were responsible for the improved cleaning in all three areas. These alkyl benzene sulfonic acid surfactants are not neutralized with alkali metal, alkaline earth metal, or ammonium salts as are the typical detergents using substituted alkyl benzene sulfonates.

The linear alkyl benzene sulfonic acids used in this invention are, as previously mentioned, commonly neutralized with sodium or other alkali metal salts to make common cleaners. Linear alkyl benzene sulfonic acid itself is produced by a two step synthesis, in which benzene is first alkylated with some alkyl chloride in the presence of catalyst. Next, the alkylated benzene is reacted with sulfonating reactant. A third step, which does not concern the present invention, can occur when the thus produced linear alkyl benzene sulfonic acid is neutralized with an alkali metal hydroxide, such as NaOH, to produce the sodium salt, which is commonly called "LAS."

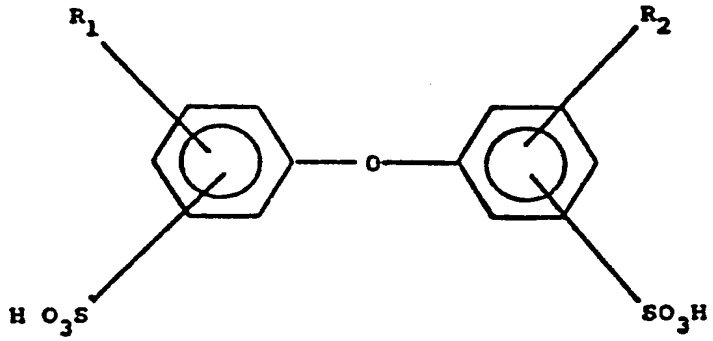
Linear alkyl benzene sulfonic acid--which was introduced for heavy industrial use, after it was discovered that branched alkyl benzene sulfonate ("ABS") was significantly less bio-degradable--is produced by many companies, including Continental Oil Company under the brand name of Conoco SA-597, and Pilot Chemical Company under the brand name Calsoft LAS-99, Witco Chemical Corporation under the brand name of Witco 1298 S ft Acid and Stepan Chemical Company under the brand name of Bio Soft S-100.

Linear alkyl benzen sulfonic acid has th g neral structur



wherein R is alkyl averaging 5 to 20 carbon atoms. Most preferable for use in the formulas of this invention are dodecylbenzene sulfonic acids, wherein R averages about 11.4 carbon atoms in length.

Other alkyl aryl sulfonic acids suitable for use in this invention include alkylated diphenyl oxide disulfonates of the general structure



wherein R_1 is H and R_2 is alkyl, averaging 5 to 20 carbon atoms in length. When R_1 is alkyl, R_2 is H.

Preferably, a range of 0.001% to 50.0% particularly, 1.0% to 30.0% and most preferably 5.0% to 15% by weight of acid surfactant is present in compositions of this inv ntion. Further, the pr ferred surfactant f this invention will cause the formulas f this invention to have pH's f no more than 6.5, and preferably, below 3.

An example of a suitable alkyl sulfonic acid is Dowfax 2AO manufactured by Dow Chemical Company corresponding to th structure immediately above when R_1 is H and R_2 averages 12 carbons.

In a further embodiment, solvents are added to the acid surfactants of this invention. Solvents appropriate for use in this invention include straight chain, primary, secondary and tertiary C_{1-10} alkanols, C_{5-10} alicyclic alcohols, C_{2-8} dialkyl ethers, C_{3-20} acyl and aryl glycol ethers and mixtures thereof.

1. Alkanols: appropriate alkanol solvents in this invention have the general formula R-OH wherein R can be a straight, or substituted carbon chain of 1-10 carbon atoms. Solvents of this type include methanol, ethanol, n-propanol, isopropanol, n-butanol, sec butanol, tert butanol, hexanol, heptanol, etc.

2. Aliphatic Cyclic Alcohols (Alicylics): Further appropriate solvents herein are ring structures such as cyclohexanol, cyclooctanol, cyclodecanol, etc. These alicyclics preferably average 5-10 carbon atoms in their ring structures.

3. Dialkyl ethers: the dialkyl ethers suitable for use as solvents in this invention have a general structure $R-O-R_1$, wherein R and R_1 are equal, and each comprise a carbon chain of at least 1. Preferably, the dialkyl ethers herein compris two to eight carbon atoms in average chain length. Exampl s f this particular gr up of solvents include dimethyl ether, diethyl ether, and dipropyl ether.

4. Glycol thers: particularly pr ferred as solv nts in this invention are the glycol ethers having the general structure $R-O-R_1-OH$, wherein R is an alkoxy of 1 to 20 carbon atoms, or aryloxy of at least 6 carbon atoms, and R_1 is an ether condensate of propylene glycol and/or ethylene glycol having from one to ten glycol monomer units. Preferred are glycol ethers having one to five glycol monomer units. These are C_{3-20} glycol ethers.

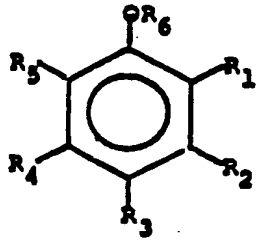
Examples of particularly preferred solvents include propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol isobutyl ether, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol butyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, diethylene glycol butyl ether, ethylene glycol phenyl ether, and propylene glycol phenol ether.

These glycol ethers are especially preferred because they are colorless liquids with mild, pleasant odors. They are very miscible with water, and have been found to be especially stable with the acid surfactants noted above.

Addition of 0.001-25.0% by weight of any of the solvents disclosed to this hard surface acid cleaner appears desirable, and especially preferred is .1 to 15% by weight of added solvent. As will be further discussed in greater detail, addition of solvents to the hard surface acid cleaners herein provides surprisingly even greater cleaning benefits.

In yet another embodiment of this invention, antimicrobial compounds are added to the novel hard surface cleaners of this invention which are selected from substituted phenols and quaternary ammonium compounds.

1. Substituted phenols: Suitable antimicrobial compounds can be selected from the substituted phenols having the general structure



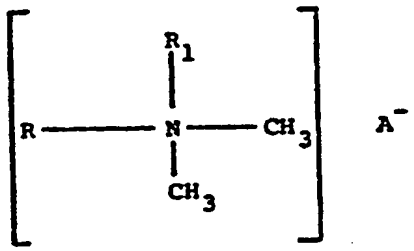
wherein R_1, R_2, R_3, R_4, and R_5 can be separately phenyl group, Cl, H, and the alkali metal salts thereof, and R_6 can be H or Na. Phenols suitable for use in this invention include those sold by Dow Chemical Company under the brand name Dowicide, such as sodium o-phenyl phenol tetrahydrate (Dowicide A), o-phenyl phenol (Dowicide I), 2,4,5 trichloro-phenol (Dowicide II), 2,4,5 trichloro-phenol, sodium salt, 1/2 hydrate (Dowicide B), and pentachlorophenol (Dowicide EC-7). Further phenols include ortho-benzyl-para-chlorophenol sold under the brand name Santophen I by Monsanto Chemical Corporation.

2. Quaternary Ammonium Compounds: particular, surprisingly effective antimicrobial compounds suitable for use in this invention are quaternary ammonium compounds.

One would normally expect that quaternary ammonium compounds, some of which are cationic surfactants, having essentially positively charged species in aqueous solution, would react with the anionic surfactants in equilibrium with the acid surfactants disclosed above and cause a precipitate to form.

However, the quaternary ammonium compounds used as antimicrobial compounds in this invention are miscible with the mixture of acid surfactant and solvent in the formula and do not precipitate. Instead, a thickening is seen to occur with a preferred percentage of up to 5.0% of quaternary ammonium compound. Surpassing 5.0% has a thixotropic effect on the cleaner, and this latter application may be suitable for use as very substantive cleaners, i.e., bathroom cleaners.

Suitable quaternary ammonium compounds include the ammonium salts of the general structure



wherein R and R_1 are alkyls of C_5 to C_{20}, and A^- is an acid stable anion. Preferred anions include Cl^-, Br^-, I^-, SO_4^-, ClO_4^-, ClO_3^-, and NO_3^-. Other anions stable in the acid surfactants of this invention are possible. R_1 can also be an alkyl benzyl group (in which case R is a methyl group). Preferably R and R_1 are both alkyl groups. Further particularly preferred are C_7 to C_{12} dialkyl dimethyl ammonium salts. Other cationic surfactants, notably other quaternary ammonium salts and tertiary amin. surfactants may be suitable for use as disinfectant compounds.

As previously discussed, it is generally unknown why the cationic surfactants used as antimicrobial compounds in this invention are compatible with the acid surfactants. One would normally usp ct that the quaternary ammonium compounds would co-pr cipitate with the anionic form of the acid surfactants. However, a proposed theory, which is not m ant herein to be binding, is that these

acid surfactants, n t being neutralized by any alkali metal salts as the more common ani nic surfactants are, may exhibit n ni nic moieties in solution which act t s lubilize the cationic surfactants (quaternary ammonium compounds) and keep them from precipitating with the anion form of the acidic surfactants herein.

Additionally, the antimicrobial compounds can apparently be used in combination. No loss in stability is seen by combining these two antimicrobial compounds. Further, either or both of these antimicrobial compounds may be present in the invention from approximately 0.001 to 15.0% by weight. Particularly preferred percentages of these antimicrobial compounds are from 0.1 - to 10% by weight.

Further, approximately 0.0001-25% by weight of further cleaning adjuvants may be added to the present invention. These cleaning adjuvants include thickeners selected from gums, resins and other polysaccharides, such as xanthan gums, starch, and mixtures.

Further cleaning adjuvants include defoamers, such as dialkyl polysiloxane polymers. Particularly preferred as the defomers are those sold by Dow-Corning under the trade name DB 100 for 100%dimethylpolysiloxane. Further defoamers may be applicable for use in this invention, including various cationic and nonionic surfactants.

Still further cleaning adjuvants include dyes, pigments, fragrances and builders. The dyes and pigments in this invention are merely limited to those which will not substantially deposit and stain the surface to be cleaned. Fragrances selected must generally be those which will not be degraded by the low pH of the hard surface acid cleaner. Builders can include many inorganic and organic builders, such as sodium ethylenediaminetetraacetate or HEDTA (hydroxyethyl ethylenediaminetriacetic acid). Further builders include many organic acids and their alkali metal salts, eg., citric acid, sodium citrate, sodium lactate, sodium maleate, etc.

Various formulations of the hard surface acid cleaners of this invention were assayed in the three soiling problem areas: (1) soap scums; (2) hard water stains; and (3) oily/greasy stains, as described in the following section, under "EXPERIMENTAL." Test methodologies and results of assays are set forth in greater detail below.

EXPERIMENTAL

A. Synthetic Soap Scum Test Preparation and Method:

A standard soap scum suspension was prepared using the following ingredients:

	wt.%
Ethyl Alcohol	85.0%
Calcium Stearate	5.0%
Distilled H_2O	10.0%
	100.0%

This suspensi n was applied and baked onto tiles which were then cleaned with vari us f rmulati ns of the hard surface acid cleaner (1) using a Gardner Wear Tester (i.e., "Scrubbing Test") and (2) by simple application according to the "Soak Test." Impartial panelists were asked to grade the cleaning of the synthetic soap scum stains by the formulations of this invention as well as the performances of competitive cleaners on a 0 to 5 scale, wherein 0 = no cleaning, 5 = total cleaning. The grading was averaged for a number of trials. These results are reported below in TABLES I,II and III. Competitive products were also tested. Grading was conducted over various time periods to show that the hard surface acid cleaners of this invention clean effectively much more rapidly than competitive products.

B. Hard Water Stain Test Methods:

Two "premixes" were prepared from the following ingredients:

Premix A	% wt.	Premix B	% wt.
*$Na_2 SiO_3 X 5H_2O$	5.0%	Distilled H_2O	73.0%
Distilled H_2O	95.0%	Ethanol	24.0%
		Calcium Chloride	2.0%
		Magnesium Chloride	1.0%
	100.0%		100.0%

*Metso 20 ® (Trademark, PQ Corporation)

Each premix was sprayed on preheated brown tiles, then baked and all wed t cool.

The tiles were cleaned by applying approximately 4 grams of vari us formulations of the hard surface acid cleaner, scrubbed and rinsed ("Scrubbing Test"). Impartial panelists then graded the cleaning results on a 0 to 5 scale, as previously discussed. Competitive products were also compared. Further, in a second test, "Soak Test," formulations were allowed to soak the target stain for time intervals of 30, 20, 10, 5, 3, and 1 minutes, or 10, 5, 3, 2 , 1 minutes and 45 seconds to demonstrate rapid cleaning efficency. The results are reported in TABLES I,II and III below. Participants noted also how quickly effective cleaning occurred at the various time intervals.

C. Oily/Greasy Soil Test Methods

The following oily/greasy soil mixture was prepared:

Wilson's Lard	60.0 grams
Wesson Oil	38.0 grams
Grumbacher Cobalt Drier	2.0 grams
(Cobalt Linoleate)	100.0 grams

This mixture was applied in a thin layer to pre-cleaned whit enamelled metal sheets (which material is the same as used for manufacturing procelain kitchen sinks) and allowed to dry (age) for approximately 24 hours.

Thereafter, each panel was cleaned via the Oil/Grease Stain "Soak Method," wherein approximately 5 grams of various formulations of the hard surface acid cleaner were applied and allowed to soak for time intervals of 30, 20, 10, 5, 3 and 1 minutes. Competitive products were similarly compared. Speed in cleaning, as previously noted, was scrutinized carefully. The results are reported below in TABLES I,II and III below.

TABLE I - Performance [9] of Hard Surface Acid Cleaner versus Competitive Products ("SOAK TEST")

Example	Formula/ Product Name	% wt.	Soap Scum Test[6]						Oily / Greasy Test[7]						Hard Water Stain Test[8]					
			10m[10]	5m	3m	2m	1m	45sec	30m	20m	10m	5m	3m	1m	30m	20m	10m	5m	3m	1m
1.	2-Butoxyethanol	5.0%																		
	HLAS[1]	5.0%	5.0	4.9	3.8	1.9	0.7	0	5.0	4.9	3.8	1.9	0.7	0	3.4	3.3	3.3	3.1	3.0	2.5
	H_2O	90.0%																		
2.	Ethanol	5.0%																		
	HLAS[1]	5.0%	4.9	4.4	4.1	2.8	1.6	0	4.9	4.4	4.1	2.8	1.6	0	3.4	3.4	3.4	3.4	3.4	2.8
	H_2O	90.0%																		
3.	DOW DBC[2]		4.1	2.8	1.1	0	0	0	4.1	2.8	1.1	0	0.1	0	1.4	1.4	1.4	1.	.3	0
4.	Lysol[3]		1.6	1.4	1.3	1.4	0.6	0.5	1.6	1.4	1.3	1.4	0.6	0.5	1.4	1.1	1.1	0.8	0.3	0
5.	Soft Scrub[4]		2.0	1.0	0.5	1.0	0	0	2.0	1.0	0.5	1.0	0	0	0	0	0	0	0	0
6.	Comet Liquid[5]		0.8	0.9	0	0	0	0	0.8	0.9	0	0	0	0	0.5	0.5	0.1	0		0

1) "HLAS" is alkyl benezene sulfonic acid, wherein R averages 10 to 14 carbon atoms.

2) "DOW DBC" is a trademark of Dow Chemical Company

3) "Lysol" is a trademark of Lehn and Fink Company

4) "Soft Scrub" is a trademark of The Clorox Company

5) "Comet Liquid" is a brand name of Procter and Gamble Company

6) Soap Scum Test was outlined in "EXPERIMENTAL," "A."

7) Oily/Greasy Soil Test was outlined in "EXPERIMENTAL," "C."

8) Hard Water Stain Test was outlined in "EXPERIMENTAL," "B."

9) Performance was graded by visual assays conducted by impartial panelists on a 0 to 5 scale, wherein 0 = no cleaning, and 5 = total cleaning. The grading was averaged for a number of trials. T st administrators did not disclose or identify what products the panelists were using.

10) "m" = Minutes.

TABLE II - Performance [6] of Hard Surface Acid Cleaners
("SOAK TEST")

	Formula/ Product Name	% wt.	Soap Scum Test[3]						Oily/Greasy Soil Test[4]						Hard Water Stain Test[5]					
			30m[7]	20m	10m	5m	3m	1m	30m	20m	10m	5m	3m	1m	30m	20m	10m	5m	3m	1m
7.	HLAS[1]	2%	4.8	4.8	4.6	3.0	2.0	0.4	5.0	3.4	3.6	3.6	1.4	0.4	1.6	1.5	1.5	1.4	1.4	1.0
8.	HLAS	5%	5.0	5.0	5.0	5.0	5.0	4.0	5.0	5.0	5.0	5.0	4.8	0.8	3.2	3.1	3.1	2.9	2.8	2.3
9.	HLAS	10%	5.0	5.0	5.0	4.8	5.0	4.0	5.0	4.2	5.0	4.6	4.2	4.0	4.0	3.8	3.2	3.0	3.0	3.0
10.	Dowfax 2A0[2]	2%	5.0	4.4	0.2	0.2	0.2	0.2	0.2	0.2	0	0	0	0	0	0	0	0	0	0
11.	Dowfax 2A0	5%	4.0	4.0	2.0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	3.4	3.3	3.3	3.1	3.0	2.5
12.	Dowfax 2A0	10%	5.0	5.0	4.8	3.4	0.4	0.2	0.4	0.2	0.2	0.2	0	0	4.3	4.0	4.0	3.8	3.2	3.0

1) "HLAS" is alkyl benzene sulfonic acid, wherein R average 10 to 14 carbon atoms.

2) "Dowfax 2A0," trademark of DOW Chemical Company, is a diphenyl oxide disulfonate, wherein R = H, and R_1 is alkyl of 5 to carbon atoms.

3) Soap Scum Test was outlined in "EXPERIMENTAL," "A."

4) Oily/Greasy Soil Test was outlined in "EXPERIMENTAL," "C."

5) Hard Water Stain Test was outlined in "EXPERIMENTAL," "B."

6) P rformance was graded by visual assays conducted by impartial panelists on a 0 to 5 scale, wherein 0 = no cleaning, and 5 = total cleaning. The grading was averaged for a number of trials. Test administrators did not disclose or identify what products the panelists were using.

7) "m" = minutes.

TABLE III - Performance[9] of Hard Surface Acid Cleaner Versus Competitive Products ("SCRUBBING TEST")

Example	Formula	% wt.	Soap Scum Test[7] (Visual Grading)	Hard Water Stain Test[8] (Visual Grading)
13.	2-Butoxyethanol	5.0%		
	HLAS[1]	5.0%	4.8	3.7
	H_2O	90.0%		
14.	Ethanol	5.0%		
	HLAS[1]	5.0%	4.8	3.5
	H_2O	90.0%		
15.	DOW DBC[2]		1.9	1.3
16.	Lysol[3]		1.1	0.9
17.	Boraxo[4]		2.6	1.3
18.	Soft Scrub[5]		2.1	4.0
19.	Comet Liquid[6]		3.8	2.3

1) HLAS is alkyl benzene sulfonic acid, wherein R averages 10 to 14 carbon atoms.

2) "DOW DBC" is a trademark of Dow Chemical Company.

3) "Lysol" is a trademark of Lehn and Fink Company.

4) "Boraxo" is a trademark of U.S. Borax and Chemical Corporation.

5) "Soft Scrub" is a trademark of The Clorox Company.

6) "Comet Liquid" is a trademark of Procter and Gamble Company.

7) Soap Scum Test was outlined above in "EXPERIMENTAL," "A".

8) Hard Water Stain Test was outlined above in "EXPERIMENTAL," "B."

9) Performance was graded by visual assays performed by impartial panelists on a 0 to 5 scale, wherein 0 = no cleaning, and 5 = total cleaning. The grading was averaged for a number of trials. Test administrators did not disclose or identify what products the panelists were using.

In TABLES IV-V, below, the effect of adding a solvent, selected from the preferred solvents discussed previously, to the hard surface acid cleaners of this invention was tested. Surprisingly, it was found that even stronger cleaning performances were obtained without any loss in formula stability.

TABLE IV - Effect of Adding Solvent to the Hard Surface Acid Cleaners ("SOAK TEST") [2,5]

Exampl	HLAS[1]	Solvent	Other Additive	Soap Scum Test [3] 30m	20m	10m	5m	3m	1m
20.	5.0%	0	0	5.0	4.2	.3	1.6	.2	.0
21.	"	0	6.01% DB-100[4]	4.8	5.0	3.6	1.8	0.4	0.4
22.	"	5.0% ethanol	0	5.0	4.8	4.8	4.2	0.6	0.1
23.	"	5.0% ethanol	0.01% DB-100	4.6	3.8	4.4	3.8	1.4	0.2
24.	"	5.0% isopropanol	0	5.0	5.0	4.0	3.0	1.2	0.2
25.	"	5.0% isopropanol	0.01% DB-100	4.8	4.8	4.4	0.6	0.6	.0
26.	"	5.0% diethyl ether	0	5.0	4.0	4.0	0.4	0.2	0.2

1) HLAS is alkyl benzene sulfonic acid, wherein R averages 10 to 20 carbon atoms.

2) "SOAK TEST" was outlined in "EXPERIMENTAL," "A".

3) "SOAP SCUM TEST" was oulined in "EXPERIMENTAL," "A".

4) "DB-100" is Dow-Corning's trademark for 100% dimethyl polysiloxane, a defoamer.

5) Perf rmance was graded by visual assays performed by impartial panelists on a 0 to 5 scale, wherein 0 = no cleaning, a 5 = t tal cleaning. The grading was averaged for a number of trials. Test administrators did not disclose or identify what products the panelists were using.

TABLE V - Effect of Adding Solvent to the Hard Surface Acid Cleaners ("SOAK TEST")[2,17]

Example	HLAS[1]	Solvent	Other Additive	Soap Scum Test[3] 10m	5m	3m	2m	1m	45 Secs.
27.	5.0%	0	0	4.8	4.8	3.6	3.0	0.4	0.2
28.	"	0	0	5.0	5.0	3.2	0.4	0.2	0.2
29.	"	0	0	5.0	5.0	3.6	2.2	0.2	0.2
30.	"	5.0% Dowanol DM[4]	0	5.0	4.8	4.8	4.8	2.8	0.6
31.	"	"	0	5.0	5.0	5.0	4.0	2.0	0.4
32.	"	5.0% Dowanol EB[5]	0	5.0	5.0	4.8	4.8	0.4	0.2
33.	"	"	0	5.0	4.8	4.8	4.1	3.4	0.6
34.	"	5.0% Dowanol DE[6]	0	5.0	5.0	5.0	3.8	0.2	0.2
35.	"	"	0	4.8	5.0	5.0	5.0	1.2	0.6
36.	"	5.0% Dowanol EM[7]	0	4.8	5.0	3.4	2.0	0.2	0.2
37.	"	"	0	4.8	4.8	4.4	3.6	0.8	0.2
38.	"	5.0% Dowanol TPM[8]	0	5.0	5.0	4.8	4.8	0.2	0.2

39.	"	"	0	4.8	4.8	2.8	0.2	0	0
40.	"	5.0% Dowanol DB[9]	0	4.8	5.0	4.8	4.8	0.2	0.2
41.	"	"	0	5.0	5.0	4.8	4.6	2.6	1.2
42.	"	5.0% Dowanol EE[10]	0	4.8	5.0	4.0	4.0	1.2	0.2
43.	"	"	0	5.0	5.0	4.8	3.8	0.8	0.8
44.	"	5.0% Dowanol PiPT[11]	0	5.0	4.0	0.2	0.2	0.2	0.2
45.	"	"	0	5.0	4.4	3.8	1.6	0	0.4
46.	"	5.0% Dowanol DPM[12]	0	5.0	5.0	5.0	4.0	0.2	0.4
47.	"	"	0	5.0	5.0	3.8	2.2	0	0
48.	"	5.0% Dowanol DPM[12]	5.0% IPA[16]	5.0	5.0	5.0	3.2	0.2	0.2
49.	"	"	"	5.0	4.6	5.0	4.6	2.8	0.4
50.	"	5.0% Dowanol PM[13]	0	4.8	3.8	4.8	2.2	1.0	0.2
51.	"	"	0	4.8	4.8	3.8	2.2	0.2	0
52.	"	5.0% Dowanol EPH[14]	0	5.0	5.0	0.2	3.0	2.0	0
53.	"	"	0	5.0	5.0	5.0	3.6	0.6	0.4
54.	"	5.0% Butyl Oxitol[15]	0	5.0	5.0	5.0	5.0	4.4	3.2
55.	"	"	0	5.0	5.0	5.0	5.0	3.4	2.4

1) HLAS is alkyl benzene sulfonic acid, wherein R averages 10 to 14 carbon atoms.

2) "Soak Test" was outlined in "EXPERIMENTAL," "A" above.

3) "Soap Scum Test" was outlined in "EXPERIMENTAL," "A" above.

4) "Dowanol DM" is Dow Chemical Company's trademark for diethylene glycol methyl ether ($CH_3OC_2H_4OC_2H_4OH$)

5) "Dowanol EB" is Dow Chemical Company's trademark for ethylene glycol N-butyl ether ($C_4H_9OC_2H_4OH$)

6) "Dowanol DE" is Dow Chemical Company's trademark for diethylene glycol ethyl ether ($C_2H_5OC_2H_4C_2H_4OH$)

7) "Dowanol EM" is Dow Chemical Company's trademark for ethylene glycol methyl ether ($CH_3OC_2H_4OH$)

8) "Dowanol TPM" is Dow Chemical Company's trademark for tripropylene glycol methyl ether ($CH_3O\left[CH_2CH(CH_3)O\right]_3H$)

9) "Dowanol DB" is Dow Chemical Company's trademark for diethylene glycol N-butyl ether ($C_4H_9OC_2H_4OC_2H_4OH$

10) "Dowanol EE" is Dow Chemical Company's trademark for ethylene glycol ethyl ether ($C_2H_5OC_2H_4OH$)

11) "Dowanol PiBT" is Dow Chemical Company's trademark for propylene glycol isobutyl ether ($(CH_3)_2\ C_2H_3OCH_2CHOHCH_3$)

12) "Dowanol DPM" is Dow Chemical Company's trademark for dipropylene glycol methyl ether ($CH_3O\left[CH_2CH\ (CH_3)\ O\right]_2H$)

13) "Dowanol PM" is Dow Chemical Company's trademark for propylene glycol methyl ether ($CH_3OCH_2CHOHCH_3$)

14) "Dowanol EPH" is Dow Chemical Company's trademark for ethylene glycol phenyl ether ($C_6H_5OC_2H_4OH$)

15) "Butyl Oxitol" is Shell Chemical Company's trademark for ethylene glycol monobutyl ether ($C_4H_9OC_2H_4OH$)

16) "IPA" is isopropyl alcohol (2-propanol)

17) Performance was graded by visual assays performed by impartial panelists on a 0 to 5 scale, wherein 0 = no cleaning, and 5 = total cleaning. The grading was averaged for a number of trials. Test administrators did not disclose or identify that products the panelists were using.

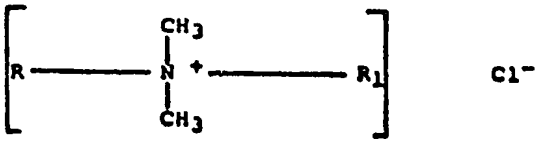
TABLE VI, below, illustrates the effect of adding a germicidal compound to the hard surface acid cleaners of this invention. As previously discussed, the preferred germicidal or antimicrobial compounds are chosen from substituted phenols, quaternary ammonium compounds, or mixtures thereof. Surprisingly, not only were the phenols stably miscible with the hard surface acid cleaners, but the quaternary ammonium compounds as well. Since the quaternary ammonium compounds are cationic species, i.e., positively charged species in aqueous solutions, it was presumed that precipitation would occur upon combination with the acid surfactants of the present invention. Surprisingly, no precipitation occurred, and the quaternary ammonium compounds also caused a thickening of the formulas when used in percentages of 5.0% or more. Adding more than 5.0% may cause a thixotrope to form, which helps the cleaning formula stay in place when applied to a vertical surface. This is a substantial benefit over other cleaners which are not as substantive and which tend to drain off. Furthermore, as disclosed in TABLE VI below, the antimicrobial activity of the antimicrobial compounds was very efficacious.

TABLE VI-Effect of Adding an Antimicrobial Compound to the Hard Surface Acid Cleaners

Example	Formula	Antimicrobial Action Against		
		Gram Positive[4] Bacteria	Gram Negative[5] Bacteria	Fungus[6]
56.	(Control)	No effect	No Effect	No effect
57.	HLAS 5.0% Ethanol 5.0% Xanthan Gum 0.1% Bardac 22[2] 0.25%	Both fresh and 60 day aged samples effective	Both fresh and 60 day aged samples effective	Fresh samples effective
58.	HLAS 5.0% Ethanol 5.0% Xanthan Gum[6] 0.1% Santophen 1[3] 0.25%	Both fresh and 60 day aged samples effective	Both fresh and 60 day aged samples effective	Fresh samples effective
59.	HLAS 5.0% Ethanol 5.0% Xanthan Gum 0.1% Bardac 22[2] 0.125% Santophen 1[3] 0.125%	Both fresh and 60 day aged samples effective	Both fresh and 60 day aged samples effective	Fresh samples effective
60.	HLAS 5.0% 2-Butoxyethanol 5.0% Xanthan Gum 0.1% Santophen 1[3] 0.25%	Both fresh and 60 day aged samples effective	Both fresh and 60 day aged samples effective	Fresh samples effective

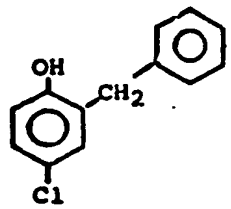
1) (Control) = 5.0% HLAS, 5.0% ethanol, and 0.1% xanthan gum. Xanthan gum is a thickener compatible with the acid surfactants of this invention

2) Bardac 22, a trademark of Lonza Chemical Company, is a quaternary ammonium compound with the following structure:



wherein R = R_1 and R averages 10 carbon atoms in length.

3) Santophen 1, a trad mark f Monsanto Chemical Company, is a ph nolic compound with the following structure:



4) Gram Positive Bacteria: Representative examples include Bacillus sp., Lactobacillus sp., Streptococcus sp., Staphylococcus sp., etc.

5) Gram Negative Bacteria: Representative examples include Escherichia coli, Salmonella sp., Proteus sp., etc.

6) Fungus: Representative examples include Trichophyton mentagrophytes, Tinea pedis (mostly Athlete's Foot fungi), etc.

Review f TABLES I-VI shows that the hard surface acid cleaners of the present invention show surprising efficacy and fast action.

In direct comparison tests with other commercially available cleaners in TABLES I,II and III, the hard surface acid cleaners showed that total cleaning was consistently achieved, whether a "Scrubbing Test" or "Soak Test" was considered, and cleaning results were achieved faster than when using any of the competitive products. TABLES IV-V disclosed the even greater cleaning efficiency when using a variety of different solvents of varying structures. Further, using more than one type of solvent as in Example 48 is possible, but in the interest of cost effectiveness may not be as desirable, although such increases still constitute a part of this invention. Lastly, TABLE VI shows that effective antimicrobial action is obtained by adding either a substituted phenol, a quaternary ammonium compound, or both, with suprisingly no loss in stability from addition of the quaternary ammonium compound.

The present invention therefore provides a multipurpose, fast acting and effective hard surface acid cleaner which is effective over the three major problem cleaning areas.

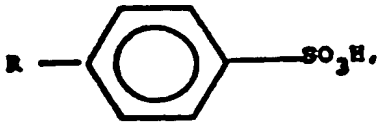
CLAIMS

1. A hard surface acid cleaner comprising:

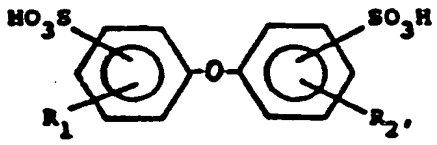
(a) alkyl aryl sulfonic acid; and

(b) at least 50.0% by weight water.

2. The hard surface acid cleaner as claimed in Claim 1 wherein said alkyl aryl sulfonic acid is



wherein R is an alkyl averaging 5 to 20 carbons atoms; or



wherein R_1 and R_2 are H or alkyl averaging 5 to 20 carbon atoms and when R_1 is alkyl, R_2 is H.

3. An all-purpose hard surface acid cleaner comprising

3. An all-purpose hard surface acid cleaner comprising

(a) an alkyl aryl sulfonic acid as defined in Claim 2

(b) a solvent selected from C_{1-10} alkanols, C_{5-10} alicyclic alkanols, C_{2-8} dialkyl ethers and C_{3-20} glycol ethers and mixtures thereof; and

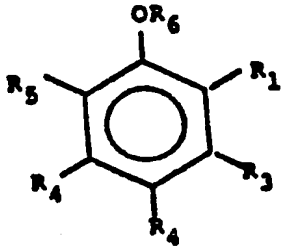
(c) at least 25.0% by weight water.

4. The hard surfac acid cl aner as claimed in any one of Claims 1 to 3 wherein said alkyl aryl sulfonic acid is present in an amount of approximately 0.001 to 50.0% by weight of the cleaner.

5. The hard surface acid cleaner as claimed in Claim 3 or Claim 4 wherein the solvent is present in an amount from approximately 0.001% to 25.0% by weight.

6. The hard surface acid cleaner as claimed in any preceding claim and comprising an antimicrobial compound selected from:

(i) a substituted phenol of the general structure:

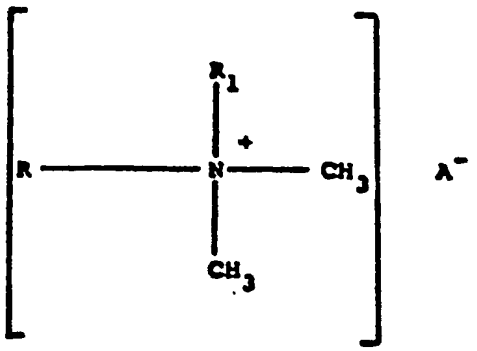


wherein R_1, R_2, R_3, R_4, R_5 can be phenyl, substituted phenyl, Cl, or H; and R_6 is H or Na;

(ii) a quaternary ammonium compound; and

(iii) mixtures thereof.

7. The hard surface acid cleaner as claimed in Claim 6, wherein the quaternary ammonium compound has the general structure:



wherein R_1 is H, or equal to R, or R and R_1 are separately alkyls of 5 to 20 carbon atoms of differing lengths, or R or R_1 is aryl of 6 to 20 carbon atoms, or alkylaryl of 7 to 20 carbon atoms, and A^- is an acid stable anion.

8. The hard surface cleaner as claimed in claim 6 or claim 7 wherein said antimicrobial compound is present in an amount from approximately 0.001 to 15.0% by weight.

9. The hard surface acid cleaner as claimed in any preceding claim further comprising a thickener selected from gums, resins, polysaccharides, and mixtures thereof.

10. The hard surface acid cleaner as claimed in any preceding claim further comprising a defoamer selected from dialkyl polysiloxane polymers.

11. A method of making a hard surface acid cleaner, as claimed in any preceding claim comprising combining the alkyl aryl sulfonic acid, water and, if required, a solvent as defined in Claim 3.

12. A method for cleaning hard surfaces having soiling materials thereon comprising contacting said hard surfaces with a hard surface acid cleaner as claimed in any one of claims 1 to 10; and removing the soiling materials and the hard surface acid cleaner from the hard surfaces.